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CHEMICAL REACTIVITY AND SYNTHESIS AT CRYOGENIC TEMPERATURES^a

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Research at Extremes of Environment

There have been many national and international scientific and technological gatherings in recent years in which the subject of discussion has centered around physical and chemical investigations at extremes of environment. Phenomena at extremely high pressures, at very high temperatures as well as studies at cryogenic temperatures have each attracted the attention of many in the scientific community because of the dual significance of much of the work to both the fundamentalist who is interested in understanding nature and to the applied scientist who is concerned with the useful aspects of the products and phenomena that may be produced.

Present technology permits experimentation at steady-state pressures of up to about 400,000 atm. (1)^c. By such techniques, workers have converted graphite into diamond, studied the miscibility of quartz and water, produced metallic sulphur, and performed many other just as exciting experiments. The solid state phase transition of feldspar into jade, which occurs at very near the temperature and pressure conditions at the Mohorovicic Discontinuity has been cited in discussions of the famous Mohole Project.

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^c Numbers in parentheses refer to literature citations in the Bibliography.

At temperatures of up to about 3500°C , a bewildering variety of unusual and largely unexpected vapor species have been observed (2). A few random examples are Si_5 , C_2 , C_3 , Cu_2 , Sn_2 , Al_2O , B_2O_2 , $(\text{KOH})_2$ and many others. These have all been identified by the use of various physical devices, the most powerful of which has been the fast inlet, line-of-sight mass spectrometer. Although the existence of more complex rather than fragmentary molecules at high temperatures may seem at first to be anomalous, this situation may be adequately explained using thermodynamic arguments. Actually most compounds that seem reasonable combinations of the constituent elements from valency considerations will likely exist in the high temperature environment. The problem is to remove this desired molecule before it is destroyed by the same environment that led to its generation. This is one of the major reasons why high temperature chemical syntheses have been, for the most part, disappointing. However, the possibility of producing new materials with interesting properties by the judicious choice of parent substance (probably combined with some sort of rapid quench technique) is certainly evident and is a current vigorous research interest.

A third exotic type of synthesis arrangement involves fission-chemistry in which the chemical reactor contains fissionable material suspended in the reactants (3). Here up to 84 per cent of the energy released in a fission is recoil energy which is deposited in a narrow track where it may dissociate or excite reactant species which then combine to form the desired product. The synthesis of N_2H_4 from NH_3 by this technique is promising, but the whole area is, like the others mentioned here, in its infancy.

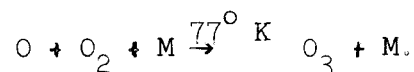
Historical Perspective

Chemistry at cryogenic temperatures is both a very old and a very new field of inquiry (4) (5). Although the first observation of chemical reactivity, or more properly the lack of it, was reported by Dewar in 1885 with his observation that neither P, Na, K, H_2S , nor HI would react with liquid O_2 ; the field has not received wide attention. For a study to have maximum significance, it is necessary to follow the reaction or to characterize the products at the low temperature, since the new products and unusual effects often depend on the maintenance of the low temperature for their existence. The more easily obtained analysis of the products after warming to room temperature is often related to the chemistry at the low temperature in a complex and unknown manner due to the reactions which occur during warmup. Most experiments have been of this more qualitative or indirect nature, but it has seemed worthwhile to mention several of them in this review.

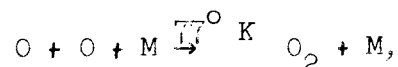
Sometime after Dewar's initial experiments, Henri Moissan (the discoverer of fluorine) came to the Royal Institution and he and Dewar performed some interesting and still controversial low temperature chemical reactivity studies with fluorine and hydrogen. They found that hydrogen gas would ignite when bubbled beneath the surface of liquid fluorine ($85^\circ K$), and at still lower temperatures, liquid hydrogen ($20^\circ K$) and solid fluorine would explode on contact. This is a truly remarkable reactivity at such a low temperature, and, although hard to accept kinetically, it has been experimentally verified. Perhaps the reaction is related in some manner to the ortho-para hydrogen problem, and, indeed, it is now possible to look at the chemistry of liquid ortho- as well as para-hydrogen (6).

Dewar also originated the notion of trapping highly reactive intermediates produced by some high energy process by using a rapid quench to cryogenic temperatures in experiments performed in 1910. He reported that at liquid air temperatures an explosive material, presumably CS, could be frozen from the effluent gases from a glow discharge in flowing CS₂ vapor. If warmed much above liquid air temperatures, the substance would explode with an audible ping and a flash of light. From these very early studies several observations important to modern research may be made. First, the discharge was essential to the experiment. With few exceptions, it is necessary to use some activating technique to produce reactants that will enter into chemical processes at cryogenic temperatures. The reactants are usually free radicals, electronically excited species, or species otherwise possessing an inordinately high energy. This may lead to products which contain elements exhibiting an unusually high or promoted chemical valence. The several activating processes that seem most useful are (1) electric glow discharges, (2) pyrolyses, (3) photolyses, and (4) arcs and flames submerged in a suitable cryosolvent. These facts lead immediately to the second point, namely that formidable problems in experimental design arise from the mutually exclusive needs to operate a high energy generation process in close proximity to a cryogenically cooled chemical reactor. A major problem area then of modern research is that of experimental design which involves both the actual carrying out of the experiment as well as effectively instrumenting it. A third significant point is that monitoring of the reaction must be performed at the low temperature since clearly warming can destroy the species of interest.

Utilizing the discharge tube, subsequent investigators have observed the reactivity of H, N and O atoms with simple molecules and have reported mostly qualitative, but interesting, accounts of the formation of colored products which froth and decompose on warming, sometimes also exploding or emitting visible light. Discharges in mixed gaseous reactants with the discharge tube immersed in some cryogen have also led to interesting, but largely qualitative information. Ozone formation by quenching the effluent gas from a discharge in O_2 gas to 77° or to 4° K has been much studied (7) and it appears that in such a process a typically 5 per cent O atom concentration in O_2 , when quenched to 77° K, will quantitatively produce O_3 by an undoubtedly heterogeneous reaction,



Three body collisions are not prevalent enough for the reaction to be homogeneous. Presumably at some O atom concentration, the competing reaction,



would become significant, but the threshold concentration is unknown.

Pyrolysis followed by cryogenic quench has been unsuccessfully used in attempts to prepare S_2 as a cryogenic liquid which was predicted to be similar to O_2 . A hot glowing wire or refractory, when submerged in liquid air or liquid O_2 will yield O_3 but no NO. Colored modifications of metals such as red selenium, yellow arsenic, or red magnesium have been similarly produced and apparently have unusual properties.

The photolysis of liquid O_2 with production of O_3 has been known almost since the first availability of liquid O_2 . Photolysis of liquid O_2 ; F_2 solutions (which

are miscible in all proportions) results in the formation of O_2F_2 and O_3F_2 . Cryogenic photolysis is attractive since one may break a particular bond and thereby produce the particular desired reactant species directly in the cold environment. Photolysis is, however, unattractive from the point of view of quantity yield in synthesis unless a chain mechanism is involved.

Submerged arcs in liquid air produce nitrogen oxides, and, with nitrogen or oxygen dissolved in liquid argon, the technique has been used in attempting to prepare new oxides or nitrides of the electrode material. Similar attempts to produce argides of the electrode have failed, but perhaps the experiments should now be repeated since Kr, Xe and Rn compounds have in the last year become well known (8).

Submerged flames of H_2 , CO, H_2S , and C_2H_2 with the flame gases in direct contact with liquid O_2 or liquid air permit, in principle, both the quenching of reaction intermediates from the flame as well as chemical reaction between these species and the cryogen itself. O_3 , NO, N_2O_5 , SO_2 etc., have been recovered from the warmed filtrates and residues from such processes.

Modern Research

The area of low temperature chemistry sort of crept along until the early 1950's when two striking experiments caught the interest of many scientists and (also quite significantly) the interest of certain people in the government who were able to provide large sums of money for research. It was observed that when the effluent from a pyrolysis of hydrazoic acid, HN_3 , was quenched to $77^\circ K$, a blue solid was formed which on warming through $148^\circ K$ would bleach and yield ammonium azide, NH_4N_3 . The second of these "catalytic" experiments, as it were, involved the quenching of the effluent from a

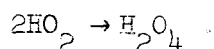
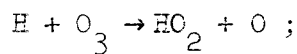
microwave discharge in nitrogen to 4.2° K. The ice that was thus formed emitted a brilliant green glow which was interrupted by intermittent blue flashes which appeared as a flame front moving through the solid material. The composition of the blue solid from HN_3 is still not understood today, but much is now known about the green and blue glowing nitrogen. Clearly energetic chemical processes can occur at low temperatures and many people felt that cryochemistry could thereby lead to new and powerful rocket fuels. With this objective, several millions of dollars were spent in this country in a unique and concerted effort to learn more about the conditions permitting the storage of high energy low molecular weight free radicals at cryogenic temperatures, i.e., species like H, N, O, OH, CH_3 , HO_2 , etc. (9). This work was centered at the National Bureau of Standards and attracted visiting workers from industry, government and universities, both from within this country and from abroad. It has been aptly said that free radical chemistry ran for a while whereas before it had only walked. Disappointingly for those who had visions of a super powerful propellant coming from this work, it has turned out that no light free radical has been prepared in concentration even remotely approaching usefulness even though virtually every experimental generation, trapping and identification technique has been investigated--at least all of the obvious ones and many of the not so obvious ones. It appears that the activation energy for the recombination of light free radicals is zero, which, if true, negates all but matrix isolation procedures and is hence rather uninteresting from the point of view of synthesis. The unpaired electron of the free radical (diradicals like O_2 have two unpaired electrons) may function as an

excellent probe which, through the application of physical analytical techniques such as electron spin resonance, nuclear magnetic resonance, optical spectroscopy, etc., have led to a much better understanding of the structure of these species and their interaction with their environment than was heretofore possible.

But, there is another whole approach to low temperature chemistry that offers much more promise for yielding product materials in useful concentrations and amounts. Whereas in free radical stabilization one arrests or stops chemical processes by means of a matrix isolation, in synthesis studies, the observation of the chemical process becomes now the essence of the experiment. In the former area one might produce carbene, CH_2 , and trap it for a detailed study by a variety of techniques. Typically, in the latter area, the CH_2 would be pumped into a cryogenic reactor and one would observe the reactions that might occur and their rates.

The kind of experiments that one may do and the nature of the results is best illustrated by looking at several current examples.

A group of Russian workers have synthesized hydrogen superperoxide by the reaction of atomic hydrogen with liquid ozone at 77°K , using a reactor as schematically shown in Fig. 1. The dark purple film of liquid ozone which is deposited on the inner walls of the reactor bleaches during contacting with atomic hydrogen that is pumped from the discharge tube. The low temperature substance has been studied by electron spin resonance, by x-ray diffraction, by calorimetry and by stoichiometry, and all results indicate that H_2O_4 does exist. It is presumably formed by the reaction sequence:



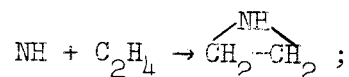
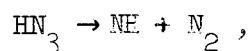
Some chemists still question this interpretation however.

The synthesis of the series of oxygen fluorides, O_2F_2 , O_3F_2 and O_4F_2 has recently been well established. These syntheses have involved a glow discharge in the mixed elements at low pressures and with the discharge tube reactor immersed in a cryogenic refrigerant, usually liquid O_2 . Each of these products is unstable and none exists at as high a room temperature. At 90°K , O_3F_2 is a blood red liquid (melting point is 82°K) rather resembling liquid bromine in appearance, and O_2F_2 is an orange-red solid which melts at 110°K . Both of these molecules will exist only as long as the low temperature is maintained, O_3F_2 decomposing above 90°K (10) and O_2F_2 above 113°K (11). Interestingly, O_3F_2 is likely the most powerful oxidizer known as it will, at liquid air temperature, ignite or explode on contact with a wide variety of substances including NH_3 , CH_4 , S, and I_2 (12). O_2F_2 is similarly reactive with the puzzling property of forming similar appearing purple compounds when reacted at very low temperatures with Cl_2 or molecules containing monovalent chlorine (13). Liquid O_2F_2 will ignite CH_4 , NH_3 , H_2O , Br_2 , PF_3 , and N_2F_4 on contact at temperatures of about 110° to 130°K , but in the same temperature region, it is unreactive toward Ca, Mg, N_2O_4 , ClF_3 and NF_3 (14). O_2F_2 reacts very strongly with red phosphorus in both a solid-solid reaction at 77°K as well as when the phosphorus is dispersed as a slurry in freon-13 (CF_3Cl) at somewhat higher temperatures.

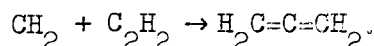
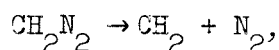
But one again finds that the nature of the low temperature chemical behavior beyond the mere observation that it occurs, and often in a striking

manner, is unknown due to the absence of data obtained at the low temperatures.

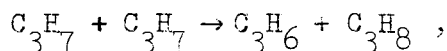
The needed direct low temperature observation of chemical reactions has been accomplished utilizing absorption spectroscopy since 1959. For example, photolysis of solid N_2 containing CH_2N_2 and CO at $20^\circ K$ readily produces ketene, CH_2CO , and with C_2H_4 rather than CO, one obtains cyclopropane. Here the reaction is observed at $20^\circ K$. In argon matrices the following processes may be observed to occur at $4.2^\circ K$ (15):



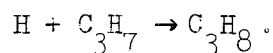
and,



It is also clear that accumulated chemical evidence on warmed products may in some instances permit reasonable, although not optimum, deductions about low temperature reactions. For example, it seems clear from experiments with deuterium that hydrogen atom addition to some olefins followed by abstraction does occur at $77^\circ K$ whereas with some other olefins this abstraction is not apparent (16). From the propylene reaction with D rather than with H atoms, it was established that virtually all of the propane was formed by:



rather than by



Evidently the isopropyl radicals are rather free to diffuse in the solid at 77° K. The rate of reaction was strictly first order with respect to propylene at up to 90 per cent conversion whether or not the reactant was diluted to a solvent to solute ratio of 10:1 with either C₃H₈ or CCl₂F₂ (16). Therefore, the H atoms are being supplied to the solid faster than they can react, and since the rate is independent of the diluent, there is no significant interaction between the reactants and the diluent. From rate studies from 77° to 90° K, the activation energy for the hydrogen atom addition to propylene is 1.5 Kcal/mole.

The large differences observed in the rates of the low temperature hydrogenation of several olefins suggest the existence of some small difference in their activation energies, an effect not previously observed in gas phase kinetics at higher temperatures. The different low temperature rates could also be a reflection of the different diffusivities of hydrogen atoms in the different solids, but experiments in which the reactive olefin was covered by a layer of an inert paraffin hydrocarbon indicated that the diffusion of the hydrogen atoms is probably not rate controlling.

In contrast with both of these, the mass spectrometer seems to represent a more generally useful and more easily understandable procedure for chemical analysis at cryogenic temperatures than does any other technique. If the objective of our experiment is to synthesize some new molecule in weighable amounts, we must demonstrate the existence of the species at the cryogenic temperature. It will also usually be convenient to investigate the effect of the concentration of the active species in an inert diluent on that species' physical stability and chemical reactivity. The enrichment or, ideally, purification of the active species is also a necessary part of the investigation. These things, as

well as the analytical aspects of the total experiment must be performed in ways not involving prior warmup of the reaction or product materials. Absolute temperature control is essential throughout the experiment. In studies in this laboratory, the apparatus shown in Fig. 2 is being developed in an attempt to meet these requirements. Except for the cryogenic aspects, this arrangement is rather like the fast inlet, line-of-sight sampling systems that were originated by Eltenton and subsequently developed by Lossing, Kistiakowsky, Herron and Dibeler and others (17). In all of these earlier arrangements it was possible to detect free radicals, and other short lived intermediates in reactions of various sorts. The time-of-flight mass spectrometer was adopted for use in cryochemistry since the absence of the magnets of a deflection type instrument makes for an open structure which is readily amenable to the assembly of complex cryogenic dewars and associated apparatus around the ion source. Some notion of the utilization of this feature may be inferred from Fig. 2. The sample gas must not "see" any temperature other than ambient prior to its dissociation, ionization and acceleration of the sample fragments into the analyzer section of the spectrometer. And here ambient may be as low as 4.2° K. The cryogenic assembly which is shown hanging from the overhead trolley in Fig. 2, is built into a piston which travels through an O-ring gland and into a vacuum lock assembly, before entering the spectrometer itself. This allows for easy withdrawal of the cryogenic unit for adjustments without the necessity of breaking up the vacuum in the main spectrometer system. As shown schematically in Fig. 3, the cryogenic assembly consists basically of two pots, [5]^d and [9], which may be independently

^d Numbers in brackets correspond to numbers on Fig. 3.

thermostated at any temperature down to about 60° K. Two L & N Speedomax H, adjustable range, adjustable zero recorder-controllers maintain the constant temperature of each pot. In this arrangement, the controller governs the power dissipated in a heater wound on the center tube of each pot which "bucks" the refrigeration that is continuously supplied by a finely controlled input of liquid nitrogen. Obtaining a fixed temperature then is a matter of manually roughly balancing these two counteracting influences, after which the controller will achieve and maintain the balance. With the two pots at different temperatures, the connecting tube [8] has impressed upon it a thermal gradient which can be made to have any desired slope, $^{\circ}$ K/cm. Every chemist is familiar with the bands of ices that are produced down the walls of a U-tube cold trap when a gas mixture is pumped through it. This effect is pronounced when the dewar around the trap is only partially full of refrigerant. This partial separation results from the differences in the vapor pressures of the several components. The theory of the gradient tube shown in Fig. 3 is merely to spread out this thermal gradient, to control it, and to take advantage of it as a rough separation technique. Such separation may be prerequisite for producing the phenomena of interest as Dewar first discovered. Although made completely of rather massive copper, the outer surfaces of the pots [5], [9]; the gradient tube [8]; and both sides of the radiation shield [7] have been given a heavy nickel plate to minimize the radiative heat leak from the environment. The central tube of both reservoirs and the gradient tube with which the reactant substances may come into contact have each been made chemically inert by lining them throughout with monel.

After a time of injecting the effluent from the high energy genesis phase of the experiment into this system (the furnace, discharge, etc., is mounted in

the enlarged inside diameter of the higher temperature pot [5]), assume that a series of bands of enriched species have been produced in the tube [8]. Now by appropriate manipulations of the temperature of the two refrigerant chambers, first the highest vapor pressure substance, and then the next highest, and so on may be moved down the tube and into the lower temperature reservoir [9]. This reservoir has an extension [11] which is advanced directly into the ionization chamber of the spectrometer. This extension, made of high thermal conductivity copper, is at essentially the same temperature as is the pot itself (calculations indicate a maximum ΔT of 0.9° K). The monel hypodermic delivery tube [1] which is 0.020 in. inside diameter by 3 in. long, conducts the sample gas from the main volume of the trap into the ionization space of the spectrometer. The exit end of the tube [12] injects the sample directly into the ionizing electron beam since when in operating position, i.e., with the extension advanced into the ion source, the electron beam makes grazing tangential incidence with this exit port. A fast pumping system (750 l/sec.) maintains the background spectra at a sufficiently low value.

This assembly is, or will soon be, used in investigations of the stability of the dihalocarbenes, the possible free existence of the hydrides, BH and BH_3 at cryogenic temperatures, the synthesis of krypton fluorides, the reactivity of H, N and O atoms with simple molecules in the condensed phase at cryogenic temperatures, and the condensation of unusual vapors over ordinarily low vapor pressure parent substances which have been heated to rather high temperatures.

The carbenes, CX_2 , are interesting because the species enter into such a wide variety of reactions, but the chemistry of the species has never been observed directly because they have never been prepared as reagents. There has already

been one report of the preparation of liquid CCl_2 which however had to be later retracted (18). The initial claim was based on indirect data.

Both BH and BH_3 exist in the vapor phase but neither are now known as separate entities in the condensed phase (19). The species are being made by the pyrolysis of B_2H_6 and by the reaction of atomic H with films of metallic boron.

Studies of the reactivity of atomic H , N and O with a second reactant in liquid form or dissolved in a suitable cryosolvent will make more definitive some of the very interesting but qualitative observations of as much as 25 years ago. The second reactant is here composed of those elements that are high in cosmic abundance. The ultimate objective is a better understanding of certain cosmochemical problems, some of which are mentioned later in this discussion.

As mentioned earlier, the vapor over many subliming solids or boiling liquids contains unusual molecules, and the possibility of obtaining some of these as stable chemical entities by cryogenic techniques is an exciting one. We are presently working with the alkali metals, the vapor of which contains high concentrations of dimers. Na_2 which has a $^1\Sigma$ ground state is present to 17 mole per cent over liquid Na at its normal boiling point of 883°C (20).

Applications

Synthesis is and will remain the essence of applied or, more particularly, industrial chemistry. Hence, the most significant potentiality of cryochemistry here is that it presents a new dimension of preparative chemistry. One might categorize the synthesis possibilities as either (1) the preparation of completely new molecules, (2) the preparation or condensed phases of species that are ordinarily observed only in the gas phase and usually at very high temperatures; and (3) possible better routes to known substances.

One of the more interesting applications of cryochemical synthesis involves high energy chemical rocket propulsion. The primary property that one desires in a fuel-oxidizer propellant combination is a high specific enthalpy of the flame gases. Low temperature chemical synthesis offers promise in this direction because of its potentialities in the preparation of (a) endothermic molecules, (b) of stabilized free radicals, and (c) of stabilized excited electronic states or compounds involving electronically excited species. Table I gives an indication of the relative merits of the types of systems that may possibly result from current research in low temperature chemistry.

TABLE I
Typical Propellant Performance Parameters

<u>Reaction</u>	<u>Specific Enthalpy (Kcal/gm)</u>	<u>Specific Impulse (#f/#m/sec.)</u>
JP4-LOX	270
H ₂ -LOX	412
H \leftrightarrow 1/2 H ₂	13.2	1170
He(2 ³ S) \rightarrow He(1 ¹ S)	113.8	2760
He ₂ (a ³ Σ_u^+) \rightarrow 2He (1 ¹ S)	106.3	2670

It is not at all hard to see the root of the interest in cryochemistry by those concerned with high energy propulsion. As usual, the difficulty of the successful accomplishment of the three categories of objectives listed above increases directly with the expected return on the material as a propellant.

Pure ozone difluoride has been tested as an oxidizer in small scale laboratory engines. Though this material is soluble in liquid oxygen to less than one

tenth of one per cent, this small amount is still sufficient to make the solution hypergolic with hydrocarbon fuels such as JP-4, U-DETA, and UDMH, i.e., the propellants ignite on contact thus deleting the need for a pyrotechnic igniter. This characteristic makes for a simpler propulsion system and is also important if one desires engine restart capability in space. Saturated solutions of O_3F_2 in LOX are also hypergolic with liquid hydrogen but under as yet ill defined conditions (10). These things have been done. From a more esoteric point of view, it is interesting that at a recent symposium on Advanced Propulsion Concepts, a classified paper was read on reactions of the rare or inert gases. These workers can take heart from the earlier described syntheses of rare gas compounds, even though the known compounds are not themselves of direct interest as propellants.

From a more basic chemical point of view, it is certainly true that cryochemistry presents a similar new dimension. One of the central problems of chemical kinetics involves the determination of the reaction mechanism, i.e., the series of molecular encounters which together result in the overall stoichiometric reaction. But there is much ambiguity in this process, so much so that it is sometimes said that a proposed mechanism may only be disproved, never proven. The trouble arises because the chemist does not observe but must rather postulate reaction intermediates which are usually free radicals or excited species of various sorts which have a very transitory existence and for which he has little if any direct evidence. The techniques of low temperature chemistry permit, in principle, a detailed observation of the chemical effects of these basic molecular encounters.

One of the more esoteric applications of this basic chemical information concerns those strange nomades of space, the comets. Comets are composed of a solid nucleus which may be only a few miles in diameter, a gas cloud or head surrounding

the nucleus, and, of course, the most striking characteristic of all--a long, long tail which may extend millions of miles through space. A comet may suddenly develop a halo around its head, or it may expel a jet of matter in a fine beam usually toward the sun, even though the tail points away from the sun as a result of solar or light pressure. Astrophysicists feel that the comets' nucleus is composed of frozen simple molecules formed largely of carbon, hydrogen, nitrogen and oxygen such as CH_4 , O_2 , C_2H_2 , NH_3 , etc., and also containing a portion of meteoric dust (21). This affair is then aptly called the "dirty snowball" model. Some astrophysicists feel that the comets are in some ways embryonic worlds and if we could learn more about them, we may be able to conjecture more wisely about the origin of our own planet and our solar system. The behavior of comets will be understood, if at all, in terms of low temperature chemistry.

Conclusions

In this discussion it has seemed desirable, if not necessary, to discuss fragmentary information for this seems to indeed characterize low temperature synthesis. But from it all it seems apparent that the chemistry-oriented worker is today about where the physics-oriented workers were at the time helium was first liquefied. With these newly attained low temperatures, physicists set about the very ordinary task of measuring the electrical conductivity of metals when so severely cooled. Kammerlingh-Onnes certainly was not looking for the phenomenon of superconductivity but its discovery has had a very significant influence on science (and in recent years, superconductivity has become of great engineering importance). Discoveries of similar magnitude and significance are sure to come from basically chemical investigations at these same low temperatures.

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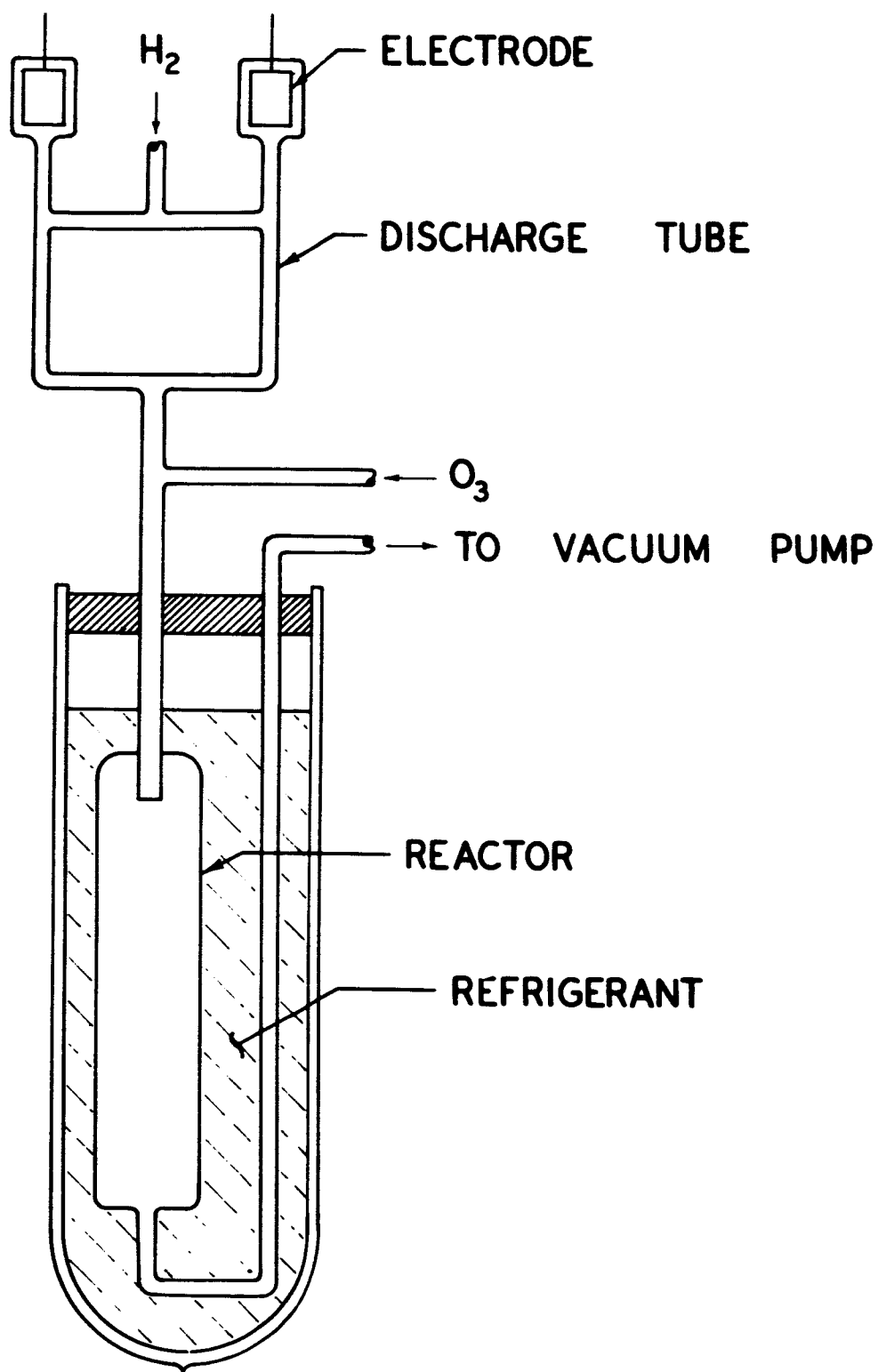


Figure 1. Apparatus of Kobozev, et al., for Production of H_2O_4
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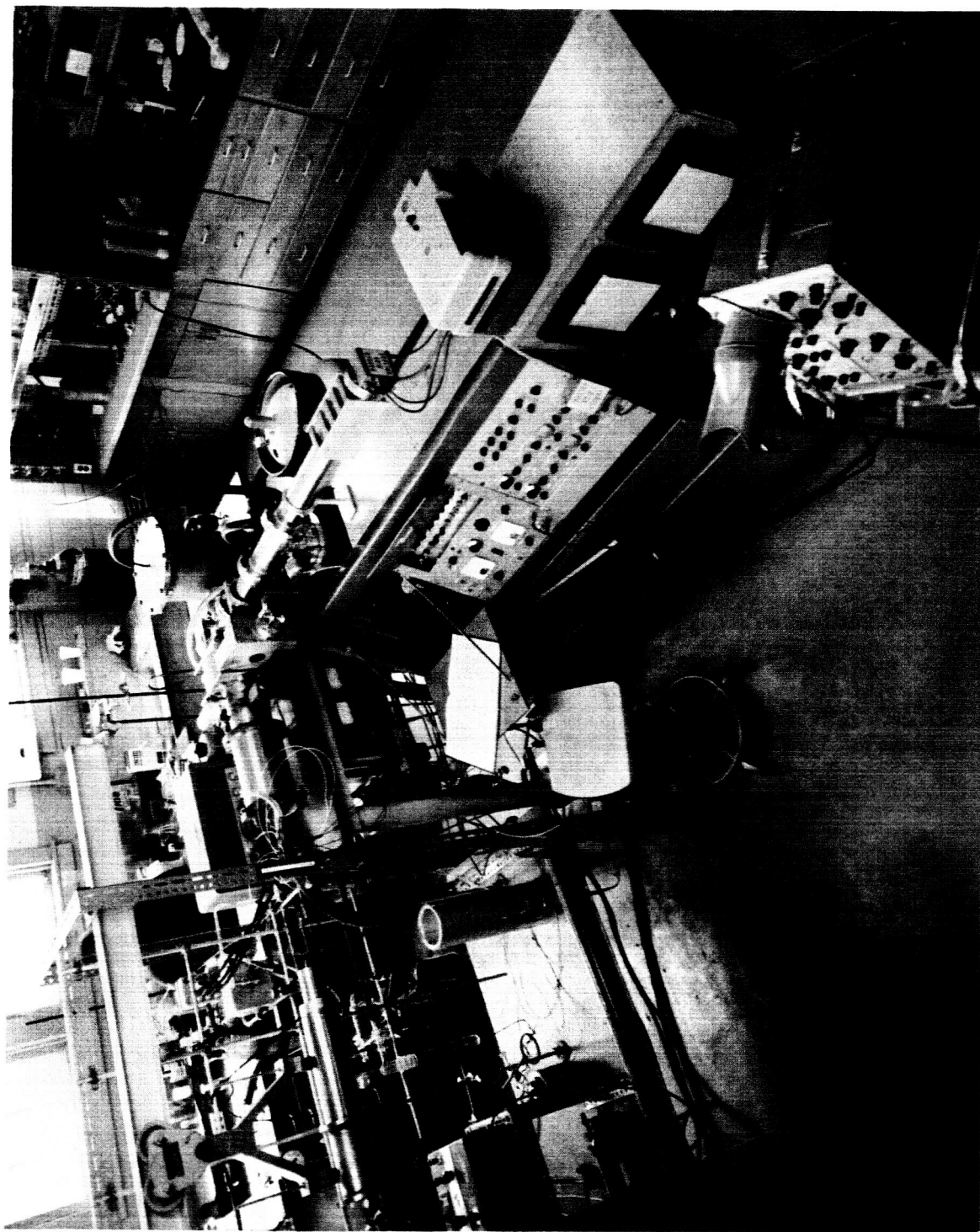


Figure 2. General View of Mass Spectrometer and Associated Equipment.

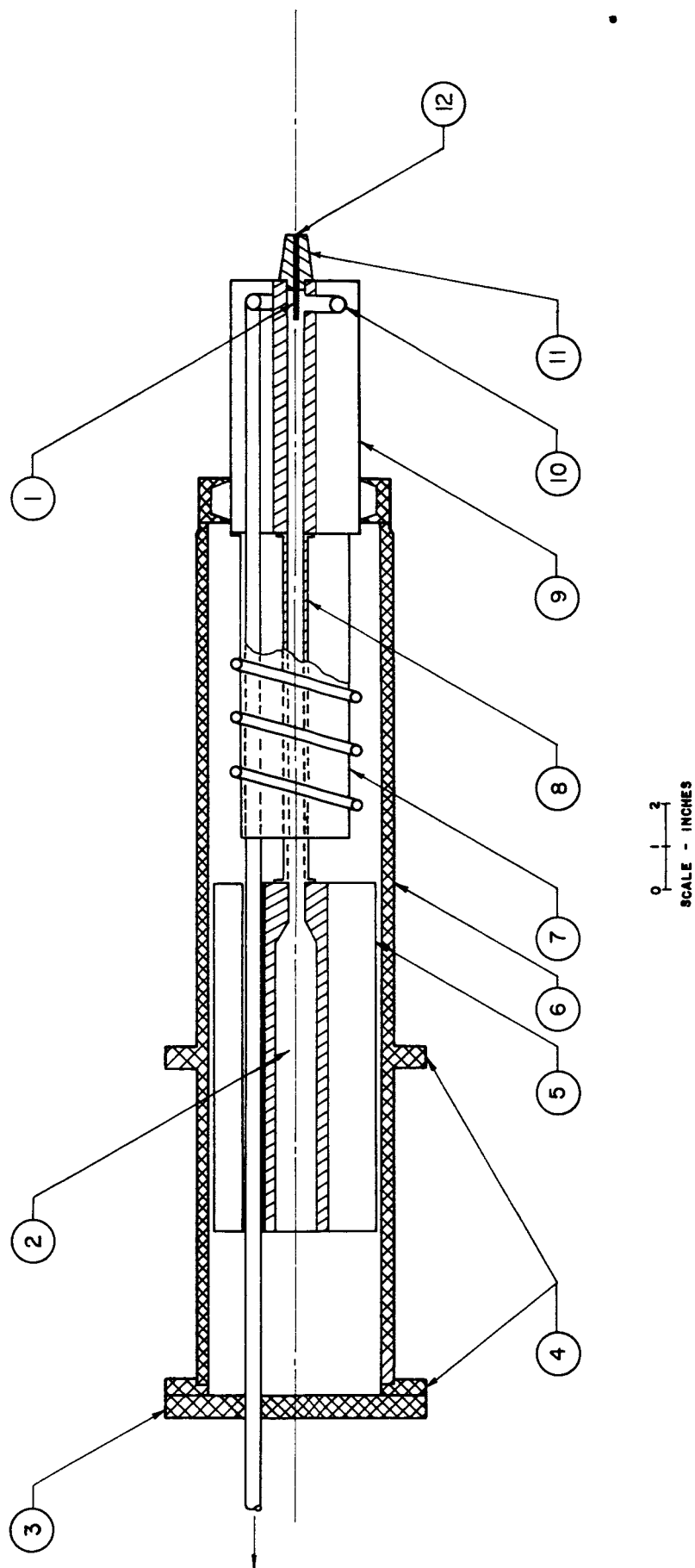


Figure 3. Schematic Diagram of Thermal Gradient Freeze-Out Assembly and Cryogenically Cooled Mass Spectrometer Sample Inlet System.